Investigation of Water Absorption in Clay-Reinforced Polypropylene Composites

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Review article

Investigation of water absorption in clay-reinforced polypropylene nanocomposites

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ABSTRACT

The behaviour of polypropylene nanocomposites containing different amounts of commercial nanoclay upon exposure to distilled water and sea water at different temperatures was investigated and compared with that of neat polypropylene. In the initial stages, the weight gain (moisture absorption) follows Fick's second law, but at longer times deviations are observed owing to physical degradation and in some cases a loss of mass. Distilled water diffuses more rapidly than sea water. As the nanoclay content increases, both the rate of moisture absorption and the maximum moisture content increase, owing to the hydrophilic nature of the nanoclay and the added compatibilizing agent. Although the moisture absorption decreases the flexural properties of both the nanocomposites and neat PP, because the unexposed (as-moulded) nanocomposites are significantly superior to the neat PP they remain so even after prolonged exposure.

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1. Introduction

Polymer nanocomposites are polymers that have been reinforced with small quantities of nano-sized particles (nanofillers). These materials represent a radical alternative to conventional filled polymers or polymer blends. In contrast to conventional composites, where the reinforcement is on the order of micrometres, polymer nanocomposites are exemplified by discrete constituents on the order of a few nanometres.

An important class of nanofillers involves nanoclays belonging to the smectite group, such as montmorillonite. Montmorillonite belongs to the family of 2:1 layered silicates. Its structure involves layers about one nanometre thick, each of which consists of two tetrahedral silica sheets fused to an edge-shared octahedral sheet of aluminium/magnesium oxide/hydroxide. To produce nanocomposite materials with optimum properties and performance, these nanoclays must be intercalated with the polymer matrix and also completely exfoliated. However, because these nanoclays are hydrophilic by nature, it is not always easy to accomplish their exfoliation in a hydrophobic polymer matrix like polypropylene (PP). The process, however, can be facilitated if the clay is treated with an organic intercalant like an onium salt, which replaces the metal cations located between the layers and increases the interlayer spacing. This aids further separation and eventual exfoliation when the treated clay is mixed with molten polymer in a melt-processing procedure. The process is further aided by incorporating into the hydrophobic polymer matrix a compatibilizing agent (CA) that resembles the matrix but also contains polar groups that lead to better interaction with the clay. For PP, the most commonly used CAs are based on maleic-anhydride-grafted polypropylene (MAgPP).

It is known that nanocomposite materials can be processed by traditional melt-processing methods. The processing of these materials is important in determining their final morphological properties. Mixing facilitates nanoscale dispersion and can lead to clay and/or polymer alignment. The degree of shear during moulding determines not only the degree of clay alignment, but also the degree of polymer orientation. For example, as expected, extruded nylon sheet with a draw ratio of 4:1 had a higher modulus than a sheet processed by injection moulding [1]. This may be due to a higher degree of platelet and polymer orientation and is a common phenomenon in the drawing of nylon. In the case of injection moulding, the clay platelets can also enhance the alignment of the polymer chains [2]. According to Kojima et al. [3], the extent of such alignment is governed by the degree of shear and can vary across the thickness of the injection-moulded parts.

The addition of nanoparticles in semi-crystalline polymers was found, in general, not to affect considerably the crystallinity of the resulting nanocomposite materials, even though there may be

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some changes in particular nanocomposite systems. It has been proposed, however, that these particles produce a much larger number of nucleating sites and in turn greatly reduce the size of the resulting spherulites [4]. On the other hand, the glass transition temperature was sometimes found to be affected by the introduction of the nano-sized particles. Results obtained by Jordan et al. [5] confirmed that when there is good filler-polymer interaction, the glass transition temperature of amorphous polymers tends to increase with a decrease in the size of particles. For semi-crystalline polymers, the transition temperature of the amorphous phase decreases with an increase in particle concentration. For amorphous systems with poor filler-polymer interfacial interaction, the glass transition temperature decreased overall.

The physical and morphological characteristics discussed above can have a great influence on the mechanical properties of nanocomposite products [6–8]. However, their exact effects on the hygrothermal behaviour of this class of materials have not been widely discussed in the literature. In the present study, extensive work is undertaken to further understand the mechanism of moisture transport in both neat polypropylene (PP) and its nanocomposites containing different amounts of nanoclay, as well as to characterize its effect on the flexural properties of this class of materials.

2. Experimental

The materials used in this study were polypropylene (Pro-fax PDC1274 from Basell Polyolefins), the commercial nanoclay Cloisite® 20A from Southern Clay Products Inc., and two different types of compatibilizing agent (CA), namely the maleic-anhydride-grafted polypropylene (MAgPP) Polybond® 3150 from Chemtura Corp. and a proprietary CA developed at NRC-IMI, consisting of a chemically-modified MAgPP. Nanocomposites prepared with Polybond 3150 are henceforth designated NC-1 and those prepared with the proprietary CA are designated NC-2. Nanocomposites with different amounts of nanoclay were prepared by processing in a twin-screw extruder at 200 °C. In a first pass, a masterbatch containing 10 wt% clay and 10 wt% CA was processed, and then a second pass was performed with addition of polypropylene (where required) to give final clay and CA concentrations of 3, 7, and 10 wt%. The products obtained were subsequently injection-moulded to give rectangular plates of 75 mm × 25 mm × 3.2 mm. Several specimens of size 75 mm × 10 mm × 3.2 mm were cut from these moulded plates. These specimens were first dried to constant weight. In order to prevent water absorption through the sides, the sides were carefully covered with fast-curing silicone rubber adhesive. The dried specimens were immersed in both distilled water and sea water at different preset temperatures (5, 25, 45, and 85 °C). The maximum immersion time considered in this study is equal to 160 days. It should be noted that the silicone rubber film covering the lateral surfaces of the immersed specimens was renewed every day, while the sea water was renewed every month. For the water absorption measurements, the specimens were withdrawn from the water, wiped dry to remove the surface moisture, and then weighed using an electronic balance accurate to 10^{-4} g to monitor the mass change during the water absorption process. The moisture content $M(t)$ absorbed by each specimen was calculated from its initial weight (w_0) and its weight after absorption (w_t) as follows:

$$M(t) = 100\left(\frac{w_t - w_0}{w_0}\right) \tag{1}$$

The effect of the absorbed humidity on the mechanical properties of the different nanocomposite materials was characterized by flexural testing performed at 25 °C on a Lloyd Instruments material testing machine, linked to a microcomputer for data acquisition and analysis. A three-point bending test was performed according to ASTM Method D790 on samples before and after moisture conditioning. The test is done by supporting the sample at two end points, while loading it from the centre at a constant speed. The ram of the machine is displaced at a constant rate of 10 mm/min to apply the necessary force to the centre of the sample, which is supported at the two ends with a span-to-thickness ratio L/h equal to 16. Five specimens were tested for each case involved and the average properties are reported. The results obtained were generally within ±10% variation. The flexural properties considered in this study are the elastic modulus (E), the maximum stress (σ_{max}), and the strain at the maximum stress (ε_{max}). These were computed using the equations given in the ASTM method.

Infrared (IR) spectra were measured by attenuated total reflection (ATR) on the surface of the specimens by means of a Spectra-Tech "Thunderdome" accessory equipped with a germanium internal reflection element. With this accessory the sample depth probed is of the order of 1 μm. To obtain information about the state of clay intercalation, X-ray diffraction (XRD) curves were measured in reflection on the surface of the specimens with a Bruker Discover 8 powder diffractometer using CuKα radiation.

2.1. Theory of moisture diffusion in polymeric materials

In many cases, the kinetics of water diffusion in a sheet of polymer is found to follow the one-dimensional Fick's second law. In such a case, the moisture content M increases with time according to the following equation [9]:

$$\frac{M - M_i}{M_m - M_i} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2}, \exp\left[-\frac{D(2n+1)^2\pi^2 t}{h^2}\right] \tag{2}$$

where M_i is the initial weight of the moisture in the material, M_m is the weight of the moisture in that material when fully saturated, D is the diffusion coefficient, t is time, and h is the sample thickness. It should be noted that in many cases, Fick's second law cannot adequately describe water diffusion in polymeric composite materials since additional mechanisms may be involved.

Shen and Springer [10] have developed a technique for calculating the diffusion coefficient D from experimental moisture uptake data. From the slope of a plot of moisture content versus the square root of time, D can be evaluated as follows:

$$D = \pi\left(\frac{h}{4M_m}\right)^2\left(\frac{M_2 - M_1}{\sqrt{t_2} - \sqrt{t_1}}\right)^2 \tag{3}$$

where M_1 and M_2 are the moisture contents at times t_1 and t_2. These times are chosen at an early stage of the moisture absorption process, where the weight change can still be taken to vary linearly with the square root of time. By considering this coefficient D and M_m, the theoretical water gain at different immersion times of the aged specimen can be predicted using equation (2).

3. Results and discussion

In the literature, it has been shown [11,12] that the presence of clay particles in the polypropylene matrix decreases the permeability of the resulting nanocomposite materials with respect to certain solvents. This was attributed to the fact that the oriented clay platelets block the advancement of the solvent molecules and force them to follow a more tortuous path. This tortuous path mechanism was further supported by modelling work [13] and other experimental results where clay fillers with larger aspect

ratio showed a larger improvement in the barrier properties [14]. Bharadwaj [13] has proposed another explanation for such a process. He has suggested that nano-sized clay restricts the molecular dynamics of the polymer chain surrounding the clay, thus retarding the relaxation of polymer chains. The retarded relaxation, in turn, reduces the diffusion of small molecules through the nanocomposites. Similar results have been obtained by Gorrasi et al. [14] and Yano et al. [15]. These authors concluded that while the permeability decreased significantly, the amount of moisture absorbed remained mostly unchanged. Although they are outside the scope of this article, measurements of polymer and clay platelet orientation at the surface of the injected specimens by means of infrared spectroscopy in the attenuated total reflection mode have shown that the clay platelets are highly oriented parallel to the surface, in a manner similar to that observed for blown PP films [16]. This result suggests that, as discussed above, the barrier properties of our different nanocomposites during a subsequent exposure to water should be improved, by creating a maze-like tortuous path that should retard the progress of water molecules through the matrix resin.

3.1. Comparison of NC-1 and NC-2

Generally speaking, the nanocomposites NC-1 and NC-2 gave practically identical results. Consequently, in the following discussion only the results for NC-2 are reported.

3.2. Immersion in distilled water

The results for the weight gain $M(t)$ of the neat polypropylene and the nanocomposite NC-2 reinforced with different amounts of clay when immersed in distilled water at different immersion temperatures are shown in Fig. 1 as a function of square root of time divided by specimen thickness ($t^{1/2}/h$); for all samples in this study $h = 3.2$ mm. While the data in Figs. 1 and 2 have been reduced to aid Fickian data analysis, the actual maximum immersion time was 160 days as mentioned before. Up to a certain point, the data can be fitted by means of a Fickian diffusion model (equation (2)) and the fits obtained are shown as lines in Fig. 1. The values of maximum moisture gain (M_m) and apparent diffusion coefficient (D) obtained from these fits are tabulated in Table 1. Each value shown in this table represents the mean over three specimens, for which the three results generally agreed within ±5%.

It can be seen that the diffusion coefficient and the maximum moisture content both increase as the amount of nanoclay increases. The saturation time, on the other hand, corresponding to the time at the first maximum of the absorption curve, decreases upon increasing the clay content. Contrary to what has been discussed above, the experimental results obtained in this study indicate that the inclusion of the clay particles in the polypropylene matrix has decreased the barrier properties of our nanocomposite materials. Different interpretations may be proposed to explain this result. First, the clay particles used in this study are much more hydrophilic than PP, which will allow the nanocomposite materials to absorb a more significant amount of moisture when exposed to humid environments. Consequently, as the clay content increases, both the diffusion coefficient and the maximum moisture content should increase. Second, the nanocomposites contain in addition to the nanoclay the compatibilizing agent with its hydrophilic maleic anhydride groups, and the comparison is being made with neat PP, with no CA present. Third, the quality of the interfacial bonding between the clay particles and the PP matrix may influence the nature of the moisture uptake. In fact, it is believed that in the case of weak or nonexistent bonding, the interfacial zone is a privileged way for the migration of small molecules. Therefore, the diffusivity
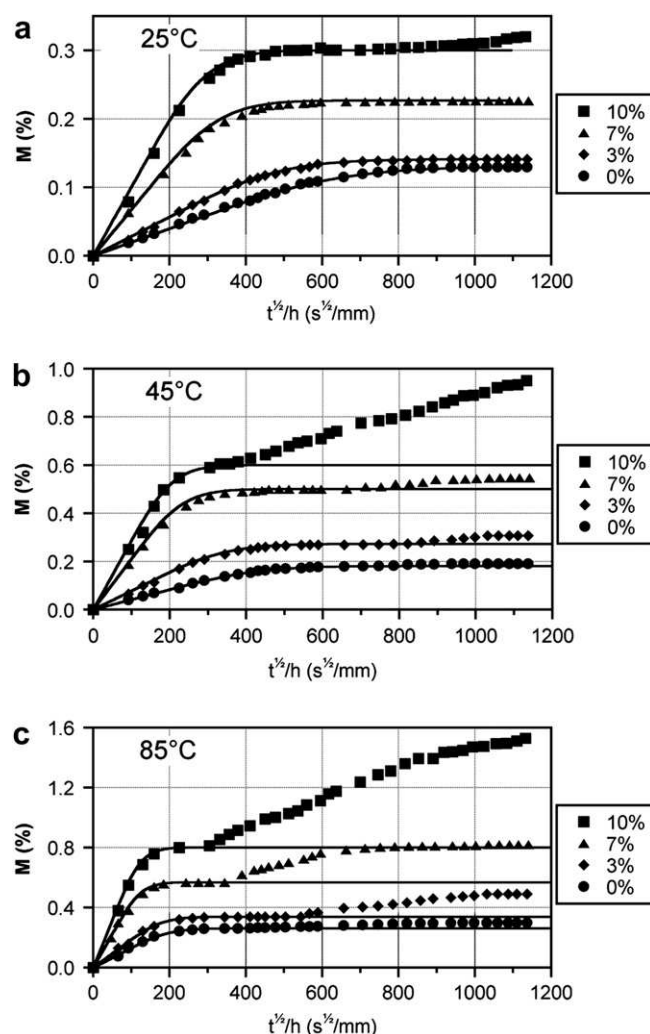

Fig. 1. Weight change as a function of time ($t^{1/2}/h$) for nanocomposite NC-2 containing different amounts of nanoclay and compatibilizing agent (0, 3, 7, and 10%) when exposed to distilled water at (a) 25 °C, (b) 45 °C, (c) 85 °C. Solid lines are fits based on Fick's law (equation (2)).

appears as an increasing function with respect to filler content. In such a case, the fillers favour the penetration of reactive agents into the specimen's interior, which should have a negative influence on durability. In the case of strong bonding, however, the interfacial zone can play a positive role during the humidity absorption process. Similar results have been obtained by Chow et al. [17] in the case of polyamide-6/polypropylene nanocomposites.

It can also be seen from Fig. 1 and Table 1 that the hygrothermal properties (D, M_m, t_s) of the different materials used in this study are also a function of the immersion temperature. For a given clay content, an increase of the immersion temperature increases both the diffusion coefficient and the maximum moisture content, but decreases the saturation time. The water diffusion in our materials is controlled by the activity of the water molecules, which is affected by the temperature [18]. Therefore, the sharp increase of the hygrothermal properties of the different materials at 85 °C from 25 °C can be attributed to the higher activity of the water molecules at 85 °C. Thus, it becomes obvious that a much longer period of time is needed to reach the equilibrium moisture content values at 25 °C, as compared to 85 °C.

At the lowest immersion temperature of 25 °C, the experimental data match the theoretical Fickian profiles quite closely throughout
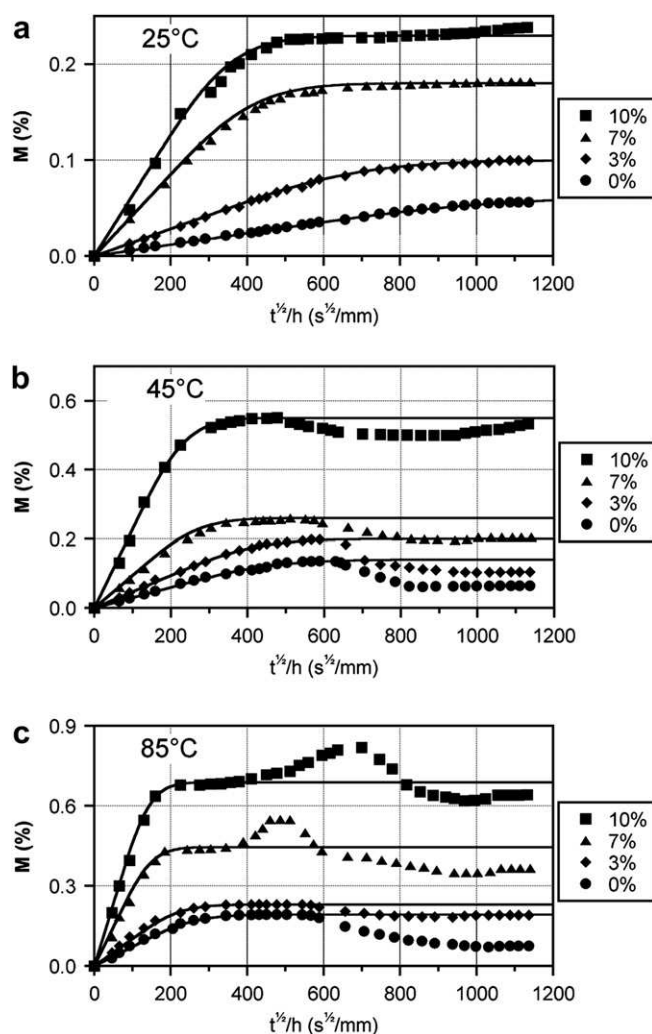
Fig. 2. Weight change as a function of time ($t^{1/2}/h$) for nanocomposite NC-2 containing different amounts of nanoclay and compatibilizing agent (0, 3, 7, and 10%) when exposed to sea water at (a) 25 °C, (b) 45 °C, (c) 85 °C. Solid lines are fits based on Fick's law (equation (2)).

the time period studied (over four months). For higher immersion temperatures (45 °C, 85 °C), the data match the theoretical profile only during the initial stage of the moisture absorption process. At longer exposure times, the experimental data deviate from the theoretical profile, indicating that the absorption process at these immersion temperatures becomes non-Fickian at longer times. The immersion time at which the deviation starts decreases as the nanoclay content increases. At that time, it is expected that both physical and/or chemical changes have occurred within the exposed material. The extent of this change increases with

increasing clay content in the PP matrix. One possible explanation of this phenomenon is that in the initial stage of the water absorption process in the nanocomposite materials, the rapid moisture weight gain is associated with gradual deformation or damage processes, for example gradual clay/PP debonding, which is often irreversible [19]. The degree of debonding increases if the nanoclay content increases in the nanocomposite materials. As a result, the deviation between the experimental and theoretical results should occur earlier and be more significant upon increasing the clay content, as indicated in Fig. 1.

3.3. Immersion in sea water

Fig. 2 shows the sea water absorption curves of the neat PP and the nanocomposite NC-2 reinforced with different amounts of nanoclay. As for Fig. 1, equation (2) was used to fit the data and determine the hygrothermal properties, which are also included in Table 1. The most noteworthy feature of Fig. 2 is that the absorption process in sea water seems to be much slower than that in distilled water, irrespective of the immersion temperature and the clay content. Similar results have been reported in the literature [20,21]. It has been suggested that the presence of dissolved salt (notably sodium chloride) may be partly responsible for the reduction of the water diffusion process in the exposed material in such an immersion environment.

Fig. 2 also shows that at low immersion temperature (25 °C), the sea water absorption process can be considered as Fickian, since good agreement is observed between the experimental and theoretical results. At an immersion temperature of 45 °C, the sea water content increases in a Fickian manner up to a certain point, but then a loss of weight is observed. Such a reduction in the weight of the immersed specimen indicates that it has experienced some form of physical and/or chemical degradation, such as breakage and leaching of polymer molecules from the specimen. It is to be noted, however, in Fig. 2 that the weight loss is not very dependent on the presence of the nanoclay particles. In fact, a similar reduction is observed for both the neat polypropylene and its nanocomposites at almost the same immersion time. It is therefore suggested that the degradation process responsible for the weight loss of our different materials takes place basically in the polypropylene matrix. For the highest immersion temperature used in this study (85 °C), the absorption process in the sea water becomes much more complex, especially in the case of the nanocomposite materials. In fact, for these materials, the absorption curves represent a two stage diffusion process with an abrupt jump in the moisture gain after the first saturation process. Such a rapid moisture gain probably results from a large deformation or damage in the exposed materials, for example matrix-clay particle debonding and/or matrix cracking. These allow the exposed specimen to absorb additional amounts of moisture, as indicated in Fig. 2. Moreover, at this immersion temperature, the jump in the absorption curves of the nanocomposite materials (particularly

Table 1
Diffusion coefficient D ($\times 10^{-6}$ mm^2/s), maximum moisture content M_m (%), and saturation time t_s (h) observed for neat PP and nanocomposite NC-2 upon immersion in distilled water and sea water at different temperatures.

Clay loading (%)	Temperature $T = 25$ °C						Temperature $T = 45$ °C						Temperature $T = 85$ °C					
	Distilled water			Sea water			Distilled water			Sea water			Distilled water			Sea water		
	D	M_m	t_s	D	M_m	t_s	D	M_m	t_s	D	M_m	t_s	D	M_m	t_s	D	M_m	t_s
0	0.46	0.13	2496	0.18	0.06	2832	1.05	0.18	840	0.90	0.14	912	5.0	0.26	336	2.80	0.19	408
3	0.80	0.14	1224	0.40	0.10	1920	1.60	0.27	648	1.10	0.2	720	6.0	0.34	240	3.90	0.23	336
7	1.75	0.22	743	1.10	0.18	1248	3.50	0.50	264	2.60	0.26	336	12.2	0.57	96	8.50	0.44	168
10	2.2	0.30	576	1.50	0.23	744	4.50	0.60	144	3.40	0.55	312	12.3	0.80	72	9.15	0.69	144

those containing a high content of nanoparticles) precedes the weight loss in the curve of the neat polypropylene. This result may indicate that the debonding process of the clay particle-PP matrix or the matrix cracking in the case of the nanocomposite materials when immersed in sea water at a very high temperature precedes the breakage and leaching of the polymer molecules from the matrix of these materials.

3.4. Arrhenius treatment

The diffusion coefficients (D) obtained for the immersion of nanocomposite NC-2 in distilled and sea water at different temperatures (Table 1) were used to estimate an activation energy for the water diffusion process by means of the Arrhenius equation:

$$D = D_0 \exp \frac{-E_a}{RT} \tag{4}$$

where E_a, D_0, R and T are respectively the activation energy for diffusion, a constant coefficient, the universal gas constant, and the temperature in degrees Kelvin. This equation can be reduced to a linear form by taking the natural logarithm of both sides. Fig. 3 is an example of the Arrhenius dependence of the diffusion coefficient with temperature for the different materials used in this study, after immersion in distilled water. From the slope $(-E_a/R)$ of the resulting curves, the activation energy (E_a) can be determined. The results obtained after immersion in both distilled and sea water are shown in Fig. 4. For distilled water, the apparent E_a steadily decreases upon introduction of nanoclay into the polypropylene, from 35.5 kJ mol^{-1} at 0 wt% nanoclay to 25.3 kJ mol^{-1} at 10 wt%. This decrease in the activation energy with increasing clay content indicates that the water diffusion in nanocomposites needs relatively little energy. This is an expected result owing in part to the hydrophilic behaviour of the clay, as discussed earlier. The same trend is observed in the case of immersion in sea water, except that the E_a values are consistently slightly higher. The presence of dissolved salt in the sea water, as stated above, may be partly responsible for this result since the electrolyte can slow the diffusion process in the exposed material. The difference in the activation energy between sea water and distilled water tends to decrease as the nanoclay content increases, from about 4 kJ mol^{-1} at 0%–1 kJ mol^{-1} at 10%. It is believed that the presence of the clay in the nanocomposite materials promotes the creation of micropores in the interface region between the PP matrix and the clay. Consequently, the effect on the diffusion process of the salt present in the sea water is eclipsed and the moisture absorption in sea
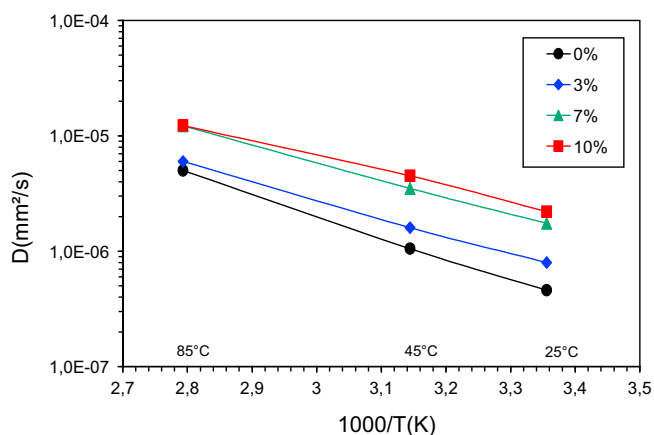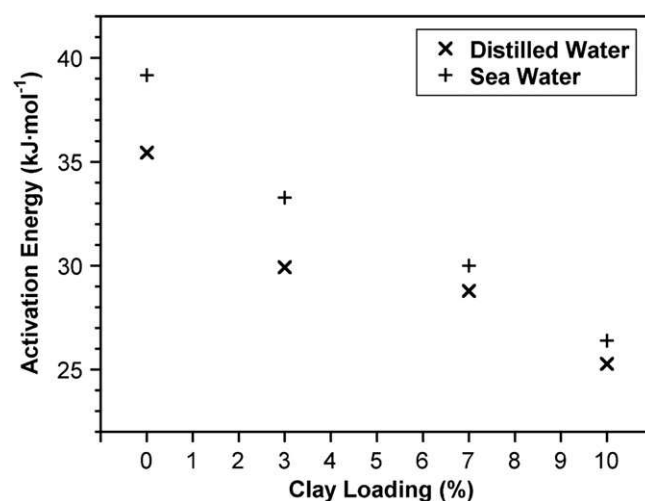

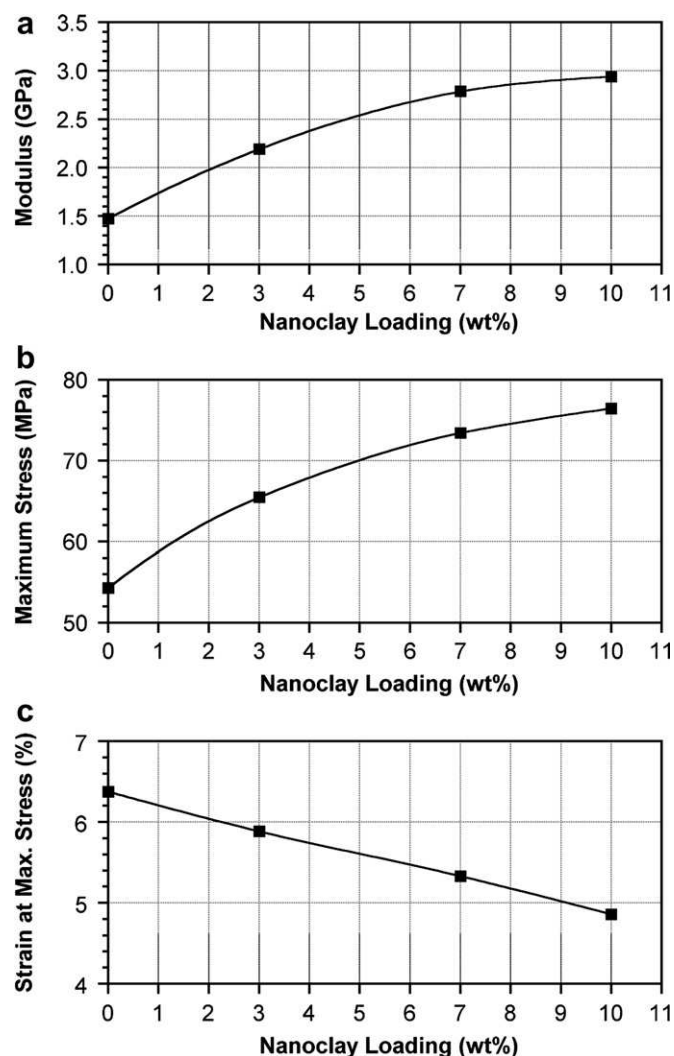**Fig. 4.** The effect of the clay content on the activation energy of the water absorption process.

Fig. 5. Mechanical properties in flexion of the as-moulded PP and nanocomposites NC-2 with different clay loadings.

Fig. 3. Arrhenius dependence of the diffusion coefficient with temperature for the different nanocomposites (0, 3, 7, and 10%).

water and distilled water tends to become more similar at higher clay contents.

3.5. Mechanical properties of as-moulded and aged nanocomposites

One of the primary reasons for adding reinforcements to polymers is to improve their mechanical performance. For example, the addition of high-modulus fillers increases the modulus and the strength of a polymer. In traditional composites, unfortunately, this often comes at the cost of a substantial reduction in ductility, and sometimes in impact strength, because of stress concentrations caused by the fillers. Well-dispersed nanoreinforcements, on the other hand, can improve the modulus and strength and maintain ductility because their small size does not create large stress concentrations. This section highlights the effect of the nanoclay content and the absorbed humidity on the flexural properties of our nanocomposites.

Fig. 5 shows the flexural properties of the as-moulded PP and the NC-2 nanocomposites with 3, 7, and 10 wt% nanoclay. Both the elastic modulus and the maximum stress increase substantially as the clay content increases. At 10 wt% nanoclay, the modulus and maximum stress increase by factors of about 2 and 1.5 respectively with respect to neat PP. However, it should be noted that the most

significant improvement is obtained between 0 and 3 wt% nanoclay content. This can be explained by the fact that at lower nanoclay loadings, somewhat better intercalation/exfoliation can be expected. At higher loadings, where there is a higher proportion of unintercalated clay, the material behaves more like a micro-composite. The role of the clay as a reinforcing agent in the poly-propylene matrix is clearly evident. Similar results have been reported in the recent literature [22,23]. According to Kojima et al. [24], a region where the polymer chains are restricted in mobility contributes to the improvement of some mechanical properties of a polymer–clay hybrid, and the elastic modulus would be one of them. Results obtained by Manias et al. [25] support these obser-vations and confirm that such improvement is caused by the volume constrained by the platelets of the clay particles. Moreover, these authors have suggested that to optimize the increase of these properties, the degree of dispersion must be optimized to maxi-mize the degree of matrix/filler interaction. The work presented by Hasegawa et al. [26] on PP nanocomposites, in which adding maleic anhydride (MA) to the matrix changed the degree of filler disper-sion, supports these hypotheses. Increasing the clay content in the
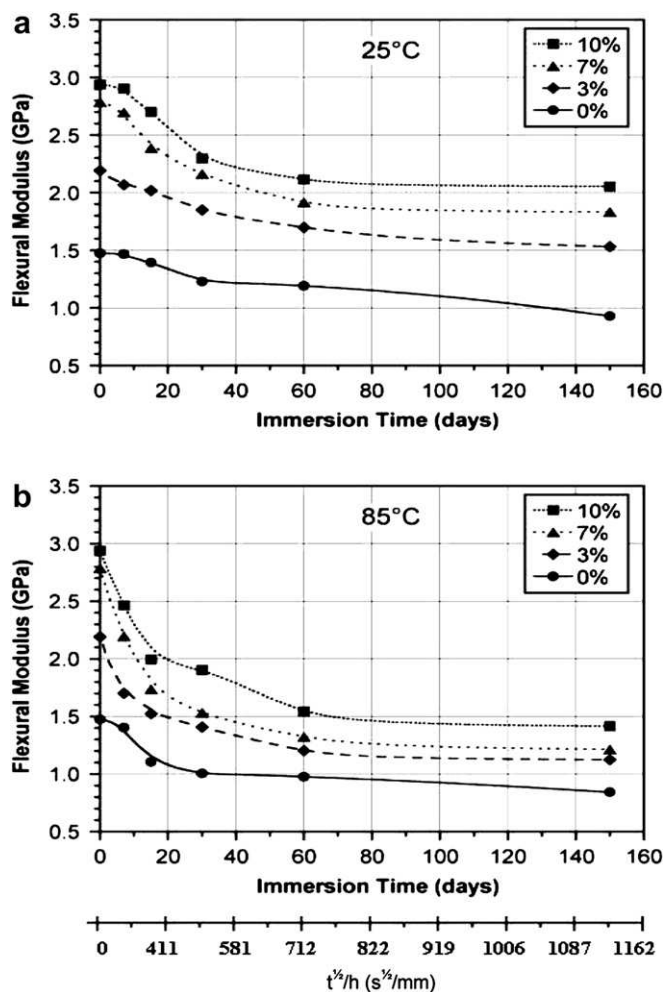

Fig. 6. Effect on the flexural elastic modulus of immersion in distilled water at (a) 25 °C and (b) 85 °C for nanocomposites NC-2 containing different amounts of nanoclay. Lines are meant as a guide to the eye.
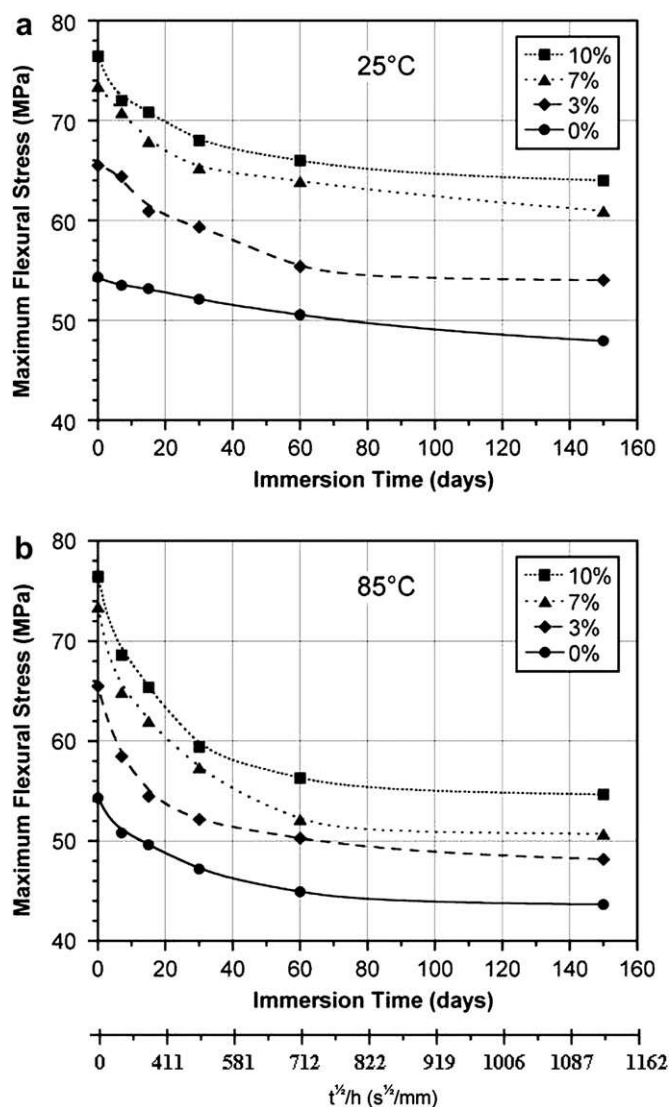

Fig. 7. Effect on the maximum flexural stress of immersion in distilled water at (a) 25 °C and (b) 85 °C for nanocomposites NC-2 containing different amounts of nanoclay. Lines are meant as a guide to the eye.

polymer matrix should therefore continuously constrain the polymer chains' mobility in the polymer matrix and some mechanical properties of the nanocomposite materials should be improved. The results in Fig. 5 confirm this tendency. Such an improvement in the elastic modulus and the maximum stress by the increase of the clay content is accompanied by a decrease of the degree of strain at the maximum stress, as also shown in Fig. 5. This decrease could be explained by the same reasoning discussed above and it is due to the decrease of the mobility of the polymer chains as the clay loading in the nanocomposites increases.

Figs. 6–8 show the effects of both time and temperature of immersion in distilled water on the flexural properties of the neat polypropylene and its NC-2 nanocomposites. These figures show a decrease of both the elastic modulus and the maximum stress and an increase of the strain at maximum stress as the amount of absorbed moisture increases. These results are to be expected. It fact, in the open literature, it is generally accepted that the mechanical properties of polymer composites involve an ability for the chain molecules present in the matrix of these materials to slip past each other. Moreover, it is recognized that the more difficult is

that slippage of the molecules, the greater will be the mechanical performance. If water, a rather reactive agent, reaches the interior of this matrix, it can react with the polymer chains, interfering with the intermolecular interaction dissecting the branches of these chains [27]. This will result in greater freedom of the polymer chains to slide over each other, and the water molecules can even lubricate the sliding motion of the chains. Consequently, the presence of water molecules in the polymer matrix contributes to an easier stretching of the intermolecular bonds when loaded and, as a result, reduces specific mechanical properties of the polymer composites. Moreover, the reinforcing clay considered in this study has, as discussed above, a hydrophilic nature. Therefore, during the moisture absorption process, the amount of moisture increases at the interface between the clay particles and the polypropylene matrix because of the wicking effects or due to the presence of voids at that interface. All these cumulative factors generate high moisture concentration and high chemical activity in the composite materials and cause a more rapid degradation of the mechanical properties of this class of materials. The increase of the strain at maximum stress (Fig. 8) could be interpreted using the same explanation. Immersion in water at a very high temperature (85 °C) accentuates the degradation of the flexural properties of the
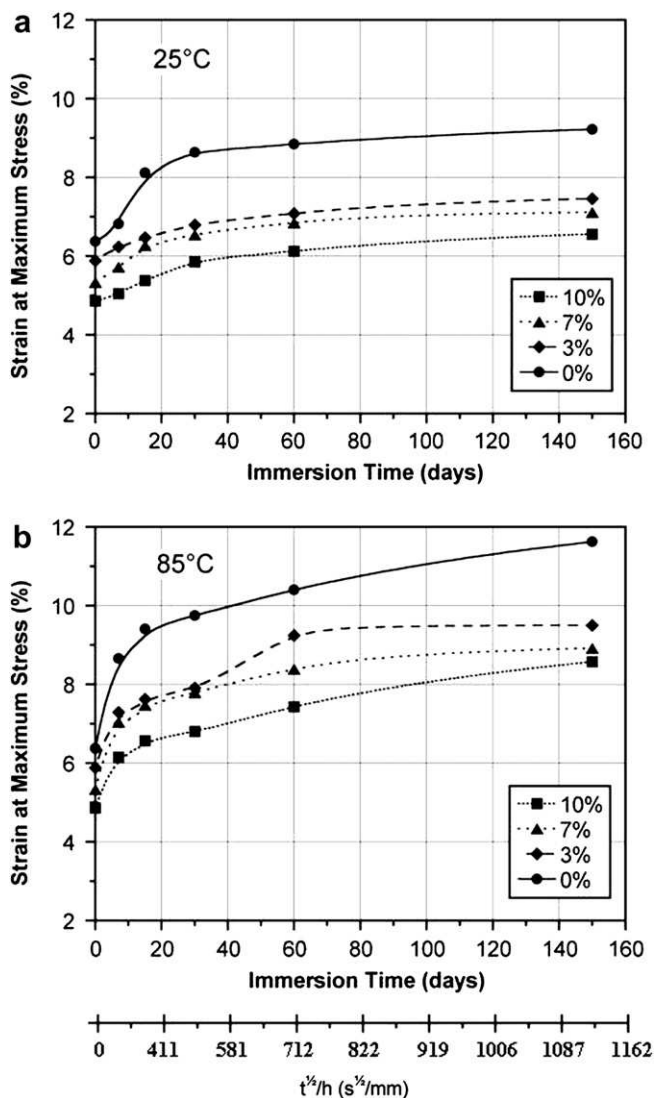

Fig. 8. Effect on the strain at maximum stress of immersion in distilled water at (a) 25 °C and (b) 85 °C for nanocomposites NC-2 containing different amounts of nanoclay. Lines are meant as a guide to the eye.
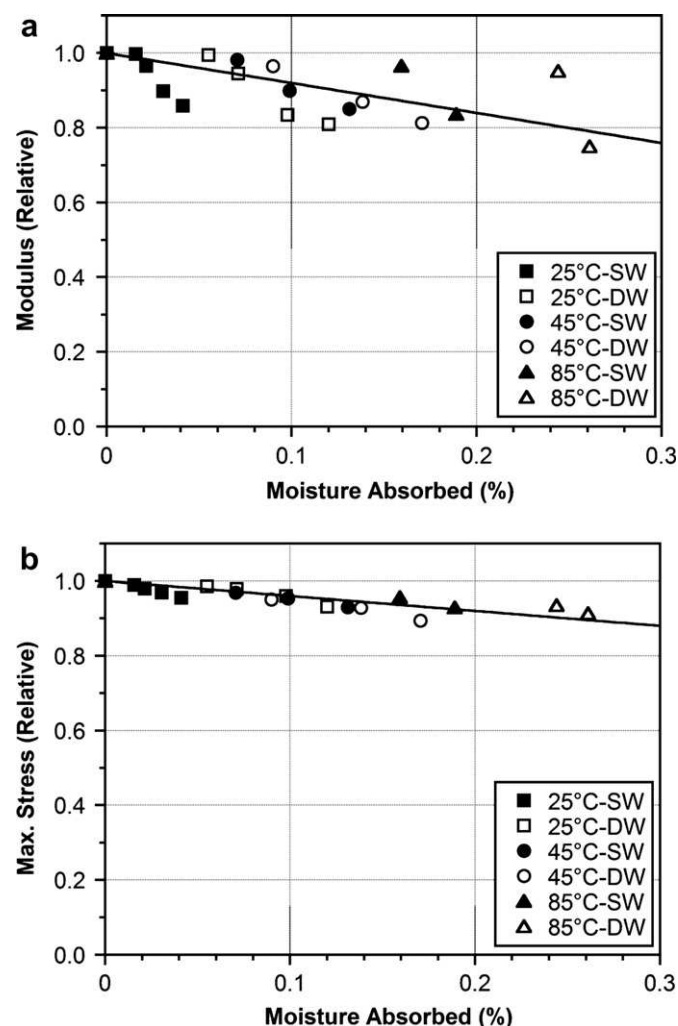

Fig. 9. Effect of the moisture absorption level on the relative flexural properties of neat polypropylene after immersion in sea water (SW) or distilled water (DW) at different temperatures: (a) modulus; (b) maximum stress.

different materials. This may be due, in part, to the higher amount of the absorbed humidity at this temperature and probably to some additional material degradation at this high immersion temperature.

Although the PP-CA-clay nanocomposites absorb water at a faster rate and to a greater extent than neat PP, it should be remembered that the properties of both deteriorate upon exposure to water. Because of the superior initial properties of the nano-composites, even after substantial exposure they compare very favourably with unexposed PP. Thus, after 150 days exposure to distilled water at 25 °C, the nanocomposite with 3% clay gives the same modulus and maximum stress as unexposed PP, as well as higher strain at maximum stress. The nanocomposites with 7% or 10% clay give even higher modulus and maximum stress, with equivalent or slightly better strain. Even at 85 °C, the nano-composite with 10% clay is still superior to unexposed PP after 60 days exposure.

3.6. Correlation of flexural properties with moisture absorption

Figs. 9–12 show how the flexural modulus and maximum stress decrease as a function of the percentage of moisture absorbed. The figures correspond respectively to nanoclay levels of 0% (neat PP), 3%, 7%, and 10%. The quantities plotted are the relative modulus E/E_0 and the relative maximum stress σ/σ_0, where E_0 and σ_0 correspond to the dry state. The data represented correspond only to samples that lie in the Fickian region of Figs. 1 and 2, before any significant physical changes like microcracking have occurred. In spite of some scatter, for a given clay content the data show a general linear downward trend. The most important factor determining the loss in properties appears to be the actual moisture content, and not the temperature at which the moisture was absorbed or the medium that provided it (sea water or distilled water). In other words, the mechanism affecting the mechanical performance appears to be rather independent of temperature or the presence of salts in the water (although these greatly affect the rate of absorption). The clay loading does seem to have some effect, however. Based on the regression lines shown in Figs. 9–12, the water contents required to give a 20% drop in modulus are 0.25% at 0% clay, 0.20% at 3% clay, 0.40% at 7% clay, and 0.82% at 10% clay. The water contents required for a 10% drop in maximum stress are very similar: 0.25% at 0% clay, 0.19% at 3% clay, 0.40% at 7% clay, and 0.59% at 10% clay. The reason for this is probably that at higher clay loadings a greater proportion of the water is absorbed within the clay and has less effect on the mechanical properties.
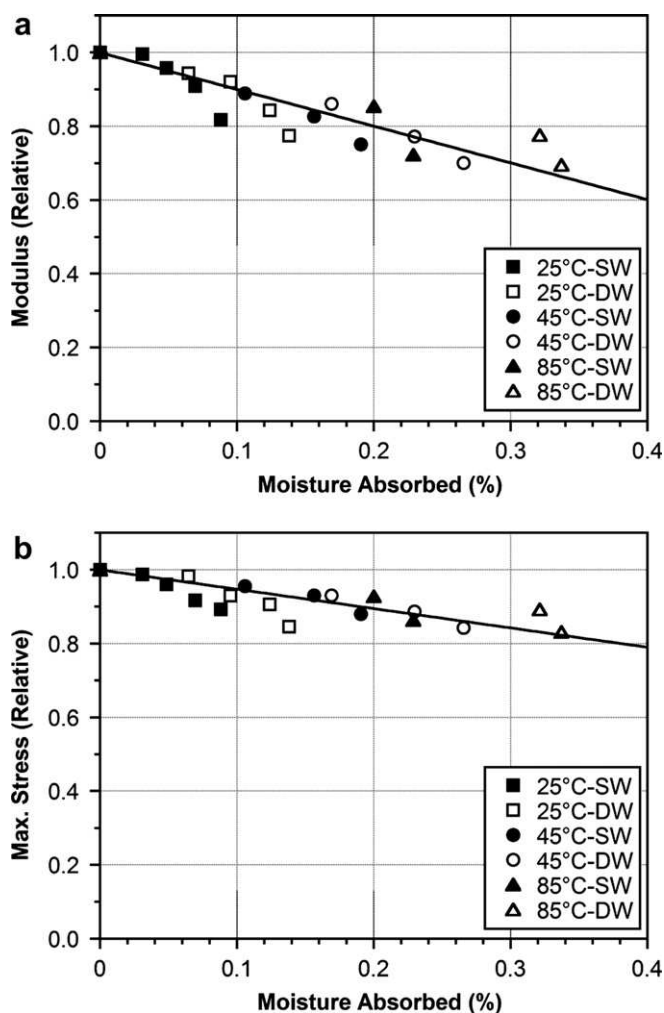

Fig. 10. Effect of the moisture absorption level on the relative flexural properties of nanocomposite NC-2 containing 3 wt% nanoclay after immersion in sea water (SW) or distilled water (DW) at different temperatures: (a) modulus; (b) maximum stress.
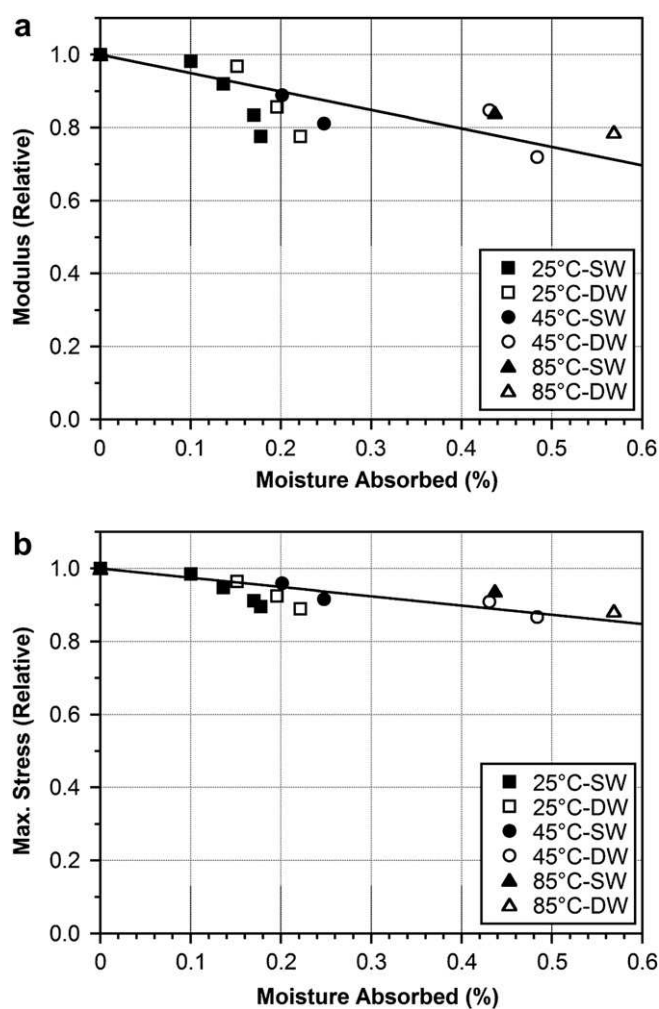
Fig. 11. Effect of the moisture absorption level on the relative flexural properties of nanocomposite NC-2 containing 7 wt% nanoclay after immersion in sea water (SW) or distilled water (DW) at different temperatures: (a) modulus; (b) maximum stress.

3.7. Physicochemical characterization

Eight exposed samples were selected for characterization by means of infrared spectroscopy and X-ray diffraction. Details are given in Table 2. Four of them contained 3% clay and four contained 10% clay. Each set of four comprised two pairs with two different water contents, and for a given pair with the same water content, one sample was exposed in sea water while the other was exposed in distilled water (for widely different times).

The infrared spectra are shown in Fig. 13 along with that of neat unexposed PP for comparison. For the samples containing 3% clay (#1−#4), in addition to the nanoclay peaks in the 1150−1000 cm^{-1} region, significant changes can be seen in the 1800−1500 cm^{-1} region of the spectrum. The peak near 1640 cm^{-1} most likely arises from the bending mode of absorbed water. In addition to this, there are distinct peaks at 1743, 1578, and 1541 cm^{-1}. These are not believed to be evidence of oxidation or degradation. The peaks at 1578 and 1541 cm^{-1} are characteristic of the carboxylate anions of calcium stearate, which is widely used as an acid neutralizer in PP. Because the amount used is generally quite small (typically 0.1%), it is not detected in the spectrum of the neat PP. The fact that the peaks are much stronger in samples #1−#4 indicates that significant surface enrichment in calcium stearate has occurred, probably through migration. The peak at 1743 cm^{-1} probably arises in

Table 2
Details of nanocomposite NC-2 specimens selected for IR and XRD analysis after immersion at 85 °C.

Specimen #	Nanoclay (wt %)	Water absorbed (wt %)	Immersion medium[a]	Immersion time (h)
1	3	0.1	DW	5
2	3	0.1	SW	24
3	3	0.2	DW	15
4	3	0.2	SW	144
5	10	0.3	DW	7
6	10	0.3	SW	12
7	10	0.6	DW	30
8	10	0.6	SW	55

[a] DW = distilled water; SW = sea water.

a similar manner, in this case from a carbonyl-containing additive, possibly an antioxidant. We have observed similar behaviour previously in nanocomposites containing 5% clay [28]. This migration is an interesting phenomenon that could influence the water absorption. It is interesting to note that the peaks in question are very weak or not detected in the spectra of the samples #5−#8 containing 10% clay. In this case, the migration appears to be inhibited by the presence of a greater amount of clay. As expected, the clay peaks at 1150−1000 cm^{-1} are more prominent in these samples. The clear presence of the out-of-plane Si−O stretching vibration at 1073 cm^{-1} is evidence of a good degree of intercalation [29]. Apart from the differences just described between the samples containing 3% clay and 10% clay, no other significant differences are observed (i.e. within each set).

The XRD curves of the eight specimens are shown in Fig. 14. Again, the only significant difference observed is between the samples containing 3% clay (#1−#4) and those containing 10% clay (#5−#8). Apart from the expected difference in intensity, there is a slight difference in peak position. For the samples containing 3%
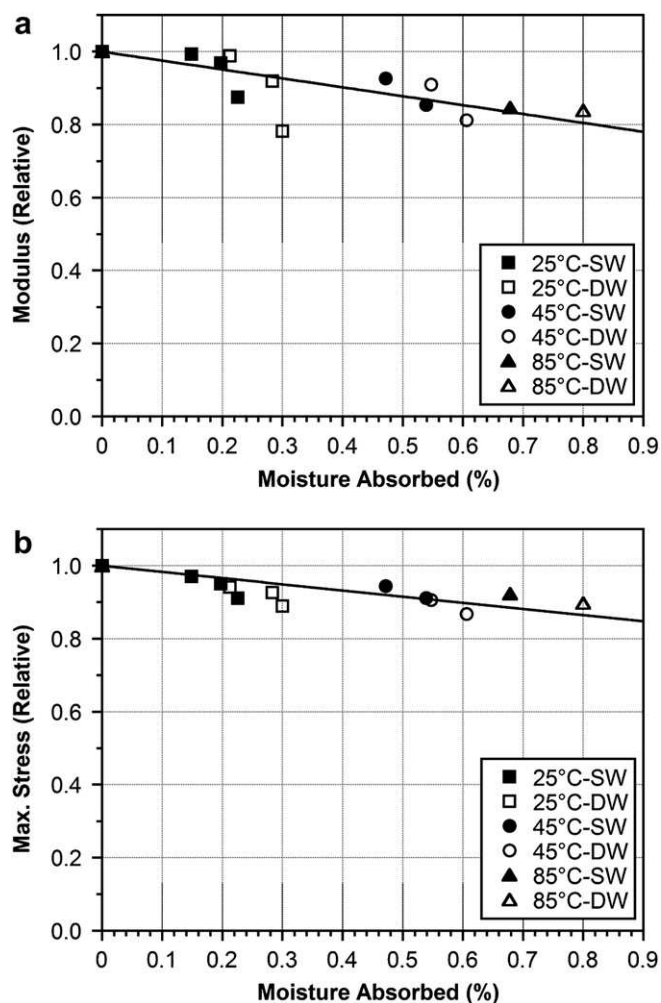

Fig. 12. Effect of the moisture absorption level on the relative flexural properties of nanocomposite NC-2 containing 10 wt% nanoclay after immersion in sea water (SW) or distilled water (DW) at different temperatures: (a) modulus; (b) maximum stress.
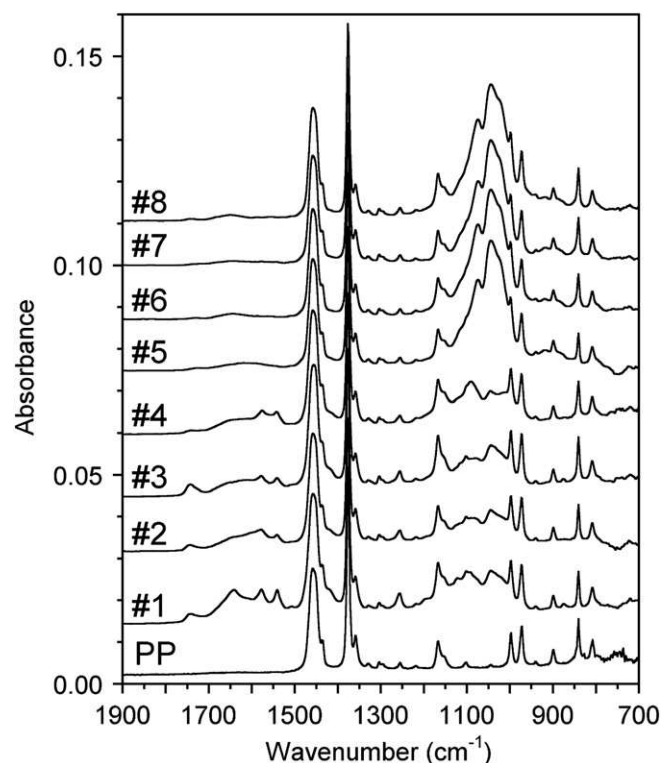

Fig. 13. Infrared spectra measured in attenuated total reflection on the surfaces of the selected samples of nanocomposite NC-2 described in Table 2.
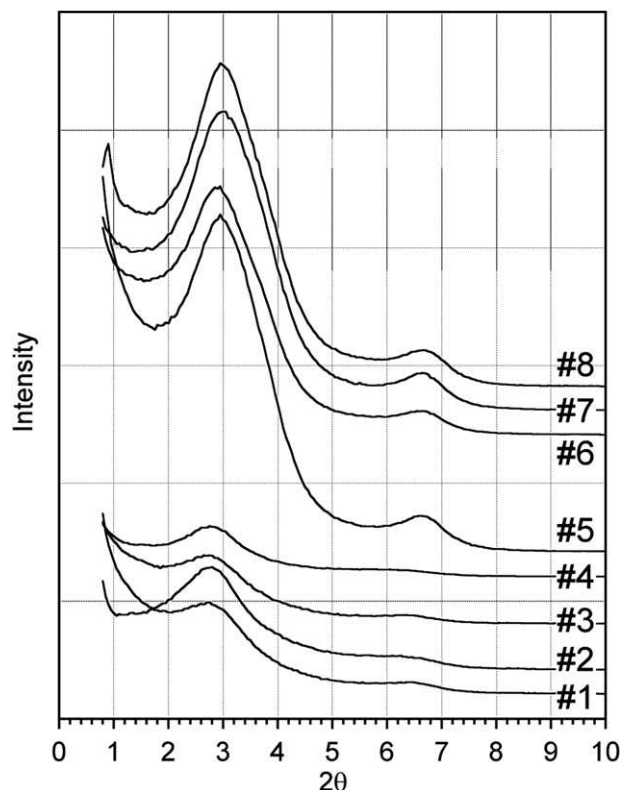
Fig. 14. X-ray diffraction curves obtained for the selected samples of nanocomposite NC-2 described in Table 2.

clay, the peak maximum occurs at $2\theta = 2.78°$, which indicates that the nanoclay is intercalated with an interlayer spacing d_{001} of 3.18 nm. For the samples containing 10% clay, the peak maximum occurs at $2\theta = 3.00°$, or $d_{001} = 2.94$ nm. A somewhat lower interlayer spacing for the higher clay loading is not unexpected, since it is well known that intercalation is harder to achieve at high clay concentrations.

It is worth noting that for the two nanocomposites used in this work, an increasing amount of absorbed moisture did not affect the d_{001} spacing. This is to be expected, since the XRD measurements are done on the outer surface of the exposed samples, which, according to the literature, saturates quite rapidly when the sample is exposed to water, so that the moisture content of this outer layer varies very little with the exposure time. Consequently, its morphology would be affected in the very first stages of the water absorption process and subsequently remain relatively constant, as seen above. Furthermore, the results presented here show that for the case where two nanocomposites have absorbed the same amount of moisture after exposure to distilled water or sea water, the interlayer spacing d_{001} is practically the same. This clearly indicates that when immersion in these two media gives the same moisture content, it should also affect the mechanical properties to the same extent, as shown in Figs. 10–12.

4. Conclusions

The present study concerning the humidity absorption process and its effect on the flexural properties of the clay-reinforced polypropylene has led to the following conclusions:

- The flexural properties of the as-moulded materials, i.e. the elastic modulus and the maximum stress, increase upon

introduction of the nanoclay particles into the polypropylene matrix. This is attributed not only to the conventional reinforcing effect of the high-modulus clay, but also to the fact that the many nanoscale particles present restrict the mobility of the matrix polymer chains in the interfacial region, thus contributing further to the improvement in mechanical properties of the polymer–clay hybrid.

- The moisture absorption process occurring upon immersion in both distilled and sea water depends on the immersion temperature. In all cases, the process is initially Fickian, and at 25 °C it remains so for over three months. At higher temperatures, the absorption deviates from the Fickian model following saturation. In the case of distilled water, the deviation takes the form of a further weight gain. In the case of sea water, it takes the form of a weight loss, or a gain followed by a loss. This was attributed to physical and/or chemical degradation of the exposed material.

- The presence of the nanoclay particles and compatibilizing agent in the PP matrix promotes the water absorption process at all immersion temperatures used in this study. This is not surprising, given that both the clay and the compatibilizing agent are more hydrophilic than the PP matrix. The clay particles can also promote the creation of micropores in the PP matrix, accelerating therefore the diffusion of the water molecules in the nanocomposite materials. For a given material, the temperature dependence of the diffusion coefficients in the Fickian region follows the law of Arrhenius. The apparent activation energy decreases with the amount of clay present, and is slightly higher for sea water than for distilled water.

- The absorbed moisture generally decreases both the elastic modulus and the maximum stress. Such reduction is due to both degradation of the nanoclay–polypropylene interface area and plasticization of the matrix. Although the nanocomposites absorb water faster and to a greater extent than the neat PP, their superior initial properties mean that even after prolonged exposure they can still show better performance than unexposed PP.

- Within the Fickian region, the percentage decrease in flexural properties appears to depend mainly on the amount of moisture absorbed, and less so on the immersion medium (sea water or distilled water) or the immersion temperature.

References

[1] Shelly JS, Mather PT, DeVries KL. Polymer 2001;42:5849.
[2] Kojima Y, Usuki A, Kawasumi M, Okada A, Kurauchi T, Kamigaito O, et al. J Polym Sci Part B Polym Phys 1994;32:625.
[3] Kojima Y, Usuki A, Kawasumi M, Okada A, Kurauchi T, Kamigaito O, et al. J Polym Sci Part B Polym Phys 1995;33:1039.
[4] Chan CM, Wu J, Li J, Cheung Y. Polymer 2002;43:2981.
[5] Jordan J, Jacob KI, Tannenbaum R, Sharaf MA, Jasiuk I. Mater Sci Eng A 2005;393:1.
[6] Wang KH, Koo CM, Chung IJ. J Appl Polym Sci 2003;89:2131.
[7] Galgali G, Agarwal S, Lele A. Polymer 2004;45:6059.
[8] Koo CM, Kim JM, Wang KH, Chung IJ. J Polym Sci Part B Polym Phys 2005;43:158.
[9] Jost W. Diffusion in solids, liquids, gases. New York: Academic Press; 1960.
[10] Shen C, Springer GS. In: Springer GS, editor. Environmental effects on composite materials, vol. 1. Westport: Technomic Publishing Co.; 1981. p. 15.
[11] Gorrasi G, Tammaro L, Tortora M, Vittoria V, Kaempfer D, Reichert P, et al. J Polym Sci Part B Polym Phys 2003;41:1798.
[12] Gorrasi G, Tortora M, Vittoria V, Kaempfer D, Mülhaupt R. Polymer 2003;44:3679.
[13] Bharadwaj RK. Macromolecules 2001;34:9189.
[14] Gorrasi G, Tortora M, Vittoria V, Galli G, Chiellini E. J Polym Sci Part B Polym Phys 2002;40:1118.
[15] Yano K, Usuki A, Okada A, Kurauchi T, Kamigaito OJ. Polym Sci Part A Polym Chem 1993;31:2493.
[16] Cole KC, Perrin-Sarazin F, Dorval-Douville G. Macromol Symp 2005;230:1.
[17] Chow WS, Abu Bakar A, Mohd Ishak ZA. J Appl Polym Sci 2005;98:780.

[18] Collings TA. Moisture absorption − Fickian diffusion kinetics and moisture profiles. In: Jones FR, editor. Handbook of polymer-fibre composites. United Kingdom: Longman Group; 1994.
[19] Weitsman YJ. Effect of fluids on polymeric composites, a review. Contract Report for Office of Naval Research, No. N00014-90-J-1556, July 1995.
[20] D'Almeida JRM. Composites 1991;22:448.
[21] Pomiès F, Carlsson L, Gillespie FW. Marine environmental effects on polymer matrix composites. ASTM STP 1230. In: Martin RH, editor. Composite materials: fatigue and fracture, vol. 5. Philadelphia: American Society for Testing and Materials; 1995. p. 283.
[22] Manias E, Touny A, Wu L, Strawhecker K, Lu B, Chung TC. Chem Mater 2001;13:3516.

[23] Zhang Q, Fu Q, Jiang LX, Lei Y. Polym Int 2000;49:1561.
[24] Kojima Y, Usuki A, Kawasumi M, Okada A, Fukushima Y, Karauchima T, et al. J Mater Res 1993;8:1185.
[25] Manias E, Chen H, Krishnamoorti R, Genzer J, Kramer EJ, Giannelis EP. Macromolecules 2000;33:7955.
[26] Hasegawa N, Okamoto H, Kato M, Usuki A. J Appl Polym Sci 2000;78:1918.
[27] Upadhyay PC, Pruez J. J Reinf Plast Comp 1992;2:198.
[28] Ben Daly H, Ben Hadj Salah H, Cole K, Denault J, Dogui A. In: Proc. Society of Plastics Engineers 65th Annual Technical Conference (SPE ANTEC 2007), Cincinnati OH, USA, May 6–10, 2007, p. 143–7.
[29] Cole KC. Macromolecules 2008;41:834–43.